JC07 Rec'd PCT/PTO 20 FEB 2002

FORM PTO-1390 (REV. 11-2000)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	1422-0519P
U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	10/049995 NEW

INTERNATIONAL APPLICATION NO.	**INTERNATIONAL FILING DATE**	**PRIORITY DATE CLAIMED**
PCT/JP00/05487	August 17, 2000	August 20, 1999

TITLE OF INVENTION
PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS

APPLICANT(S) FOR DO/EO/US
SAITO, Jun; NITTA, Hideichi; YAMASHITA, Hiroyuki; SAKATA, Yushi

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau). WO 01/14511
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is transmitted herewith.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
    1.) PCT Substitute Claims Letter w/ PCT/IPEA/409 and amended claims
    2.) Zero (0) sheets of Formal Drawings

JC13 Rec'd PCT/PTO 20 FEB 2002

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/049995	PCT/JP00/05487	1422-0519P

	CALCULATIONS	PTO USE ONLY
21. ☒ The following fees are submitted **BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . **$1,040.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . **$890.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. . . . . **$740.00** International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . **$710.00** International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	CALCULATIONS	PTO USE ONLY
Total Claims	26 - 20 =	6	X $18.00	$ 108.00	
Independent Claims	2 - 3 =	0	X $84.00	$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		Yes	+ $280.00	$ 280.00	

	CALCULATIONS	PTO USE ONLY
TOTAL OF ABOVE CALCULATIONS =	$ 1278.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.	$ 0	
SUBTOTAL =	$ 1278.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐20 ☐30 months from the earliest claimed priority date (37 CFR 1.492(f)). +	$ 0	
TOTAL NATIONAL FEE =	$ 1278.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +	$ 40.00	
TOTAL FEES ENCLOSED =	$ 1318.00	
	Amount to be: refunded	$
	charged	$

a. ☒ A check in the amount of $ 1318.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account. No. ____________ in the amount of $_______ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:

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Date: February 20, 2002

By John W. Bailey
John W. Bailey, #32,881

/cqc

PATENT
1422-0519P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant:	SAITO, Jun et al.		
Int'l. Appl. No.:	PCT/JP00/05487		
Appl. No.:	New	Group:	
Filed:	February 20, 2002	Examiner:	
For:	PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS		

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION
Assistant Commissioner for Patents
Washington, DC 20231

February 20, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/05487 which has an International filing date of August 17, 2000, which designated the United States of America and was published in English.--

IN THE CLAIMS:

Please amend the claims as follows:

4. (Amended) The process according to claim 1 or 2, wherein the inorganic powder is an alkali metal aluminosilicate.

6. (Amended) The process according to claim 1 or 2, wherein the alkali metal aluminosilicate is contained in step (A) in an amount of 5% by weight or less.

7. (Amended) The process according to claim 1 or 2, wherein the neutralization step is carried out in step (A) while blowing a gas.

8. (Amended) The process according to claim 1 or 2, wherein in step (B), a liquid binder is further added to the neutralization mixture obtained in step (A).

9. (Amended) The process according to claim 1 or 2, further comprising a surface-modifying step.

13. (Amended) The process according to claim 10 or 11, wherein the neutralization step is carried out in step (a) while blowing a gas.

14. (Amended) The process according to claim 10 or 11, wherein in step (b), a liquid binder is further added to the neutralization mixture obtained in step (a).

15. (Amended) The process according to claim 10 or 11, further comprising a surface-modifying step.

Docket No. 1422-0519P

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application.

The amendment to the claims is merely to correct improper multiple dependencies and to place the application into better form for examination. Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

Attached hereto is a marked-up version of the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By ______________________

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JWB/cqc
1422-0519P

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

Docket No. 1422-0519P

VERSION WITH MARKINGS TO SHOW CHANGES MADE

The claims have been amended as follows:

4. (Amended) The process according to [any one of claims 1 to 3]claim 1 or 2, wherein the inorganic powder is an alkali metal aluminosilicate.

6. (Amended) The process according to [any one of claims 1 to 5]claim 1 or 2, wherein the alkali metal aluminosilicate is contained in step (A) in an amount of 5% by weight or less.

7. (Amended) The process according to [any one of claims 1 to 6]claim 1 or 2, wherein the neutralization step is carried out in step (A) while blowing a gas.

8. (Amended) The process according to [any one of claims 1 to 7]claim 1 or 2, wherein in step (B), a liquid binder is further added to the neutralization mixture obtained in step (A).

9. (Amended) The process according to [any one of claims 1 to 8]claim 1 or 2, further comprising a surface-modifying step.

13. (Amended) The process according to [any one of claims 10 to 12]claim 10 or 11, wherein the neutralization step is carried out in step (a) while blowing a gas.

14. (Amended) The process according to [any one of claims 10 to 13]claim 10 or 11, wherein in step (b), a liquid binder is further added to the neutralization mixture obtained in step (a).

15. (Amended) The process according to [any one of claims 10 to 14]claim 10 or 11, further comprising a surface-modifying step.

(Rev 11/13/01)

10/049995
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DESCRIPTION

PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS

TECHNICAL FIELD

The present invention relates to a process for preparing a high-bulk density detergent composition having excellent detergency, and a small average particle size.

BACKGROUND ART

Processes for preparing powder detergents having a relatively high bulk density have been remarked.

Japanese Patent Laid-Open No. Hei 3-33199 discloses a method of producing a detergent composition comprising the steps of dry-neutralizing components in a high speed mixer/granulator at a temperature of 55°C or less, and thereafter adding a liquid binder thereto to carry out granulation. In addition, Japanese Patent Laid-Open No. Hei 4-363398 discloses a method of producing a detergent composition comprising the steps of dry-neutralizing components in a high speed mixer/granulator at a temperature of 55°C or more, and then adding a liquid binder thereto to carry out granulation.

In the processes as represented in the above publications, there are disclosed techniques for neutralizing an acid precursor of an anionic surfactant in the presence of an alkali metal aluminosilicate. However, the present inventors have found that there arise problems that the deterioration and the aggregation of

the alkali metal aluminosilicate take place by these techniques, so that the detergency of the detergent composition is lowered.

In view of eliminating the above problems, an object of the present invention is to provide a process for preparing a high-bulk density detergent composition having excellent detergency, and a small average particle size.

The above object and other objects of the present invention will be apparent from the following description.

DISCLOSURE OF INVENTION

The present invention relates to:

[1] a process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture; and

[2] a process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in

an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

BEST MODE FOR CARRYING OUT THE INVENTION

The process for preparing a high-bulk density detergent composition of the present invention is roughly classified into the following two embodiments.

[Embodiment 1]

A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture.

[Embodiment 2]

A process for preparing a high-bulk density detergent composition having

a bulk density of 650 g/L or more, comprising the steps of:

(a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

1. Step (A) or Step (a)

Step (A) or step (a) is a step in which essentially the same operations are carried out.

The liquid acid precursor of an anionic surfactant usable in step (A) or step (a) refers to those anionic surfactants in the form of acids in a liquid or pasty state at room temperature or with heating, which are formed into salts by neutralization reaction. The liquid acid precursor of an anionic surfactant includes linear alkylbenzenesulfonic acids (LAS), α-olefin sulfonic acids (AOS), alkyl sulfuric acids (AS), internal olefin sulfonic acids, sulfonic acids of fatty acid esters, alkylether sulfuric acids, dialkyl sulfosuccinic acids, and the like. The liquid acid precursors may be used in a combination of two or more components.

The amount of the liquid acid precursor of an anionic surfactant can be appropriately set depending upon the composition of the desired detergent composition. The amount of the liquid acid precursor of an anionic surfactant, as an anionic surfactant formed by the neutralization reaction, is preferably from 5

to 55% by weight, more preferably from 5 to 45% by weight, still more preferably from 10 to 40% by weight especially preferably from 20 to 40% by weight, of the final high-bulk density detergent composition. Incidentally, the present invention is effective also in a case where the main surfactant is supplied in another form in the detergent composition.

The water-soluble, alkali inorganic substance usable in step (A) or step (a) exhibits an alkaline property which can neutralize the liquid acid precursor of an anionic surfactant. The water-soluble, alkali inorganic substance described above includes sodium carbonate, sodium hydrogencarbonate, sodium silicate, potassium carbonate, calcium carbonate, and the like. Among the water-soluble, alkali inorganic substances, preference is given to sodium carbonate because the sodium carbonate can act as a detergent builder and an alkalizing agent in the final detergent composition. Therefore, it is preferable to add the water-soluble, alkali inorganic substances in step (A) or step (a) in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor of an anionic surfactant. For instance, the water-soluble, alkali inorganic substance is added in an amount of preferably from 1 to 20 times the equivalent amount required for neutralization of the liquid acid precursor of an anionic surfactant, more preferably from 2 to 15 times the equivalent amount required for neutralization, especially preferably from 3 to 15 times the equivalent amount required for neutralization.

The water-soluble, alkali inorganic substance is preferably granular, and its average particle size is preferably 30 μm or more, more preferably from 40 to 200 μm, most preferably from 50 to 100 μm, from the viewpoints of the yield improvements and the storage stability. Here, the average particle size of the

granular, water-soluble, alkali inorganic substance is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.).

In step (A) or step (a), the mixing operation is carried in the substantial absence of the alkali metal aluminosilicate. Here, the phrase "the substantial absence of the alkali metal aluminosilicate" refers to a case where the content of the alkali metal aluminosilicate in step (A) or step (a) is preferably 5% by weight or less, more preferably 3% by weight or less, of the neutralization mixture in step (A) or step (a). When the alkali metal aluminosilicate exists in a large amount in step (A) or step (a), the deterioration and the aggregation of the alkali metal aluminosilicate by the contact with a liquid acid precursor of an anionic surfactant in an acid form take place, so that the detergency performance in the resulting detergent composition is likely to be lowered thereby. Therefore, the above problem can be eliminated by carrying out the mixing operation under specified conditions of the substantial absence of the alkali metal aluminosilicate.

Incidentally, as detailed below, Embodiment 1 also encompasses an embodiment where the addition of the alkali metal aluminosilicate of step (B) is initiated at during the course of the neutralization process of step (a), or at a point where the amount of the liquid acid precursor of an anionic surfactant added exceeds a certain level.

In step (A) or step (a), besides the water-soluble, alkali inorganic substance and the liquid acid precursor of an anionic surfactant, a part or all of optional ingredients can be added. Optional ingredients which can be blended at this step include, for instance, fluorescers, pigments, anti-redeposition agents

(polycarboxylate polymers, sodium salt of carboxymethyl cellulose, and the like); surfactants (fatty acids or salts thereof, linear alkylbenzenesulfonates, alkyl sulfates, and the like); diatomaceous earth, calcite, kaolin, bentonite, tripolyphosphates, sodium sulfate, sodium sulfite, and the like.

In the case where a detergent composition comprising a tripolyphosphate as a main builder component is prepared, the average particle size of the tripolyphosphates is not particularly limited, and the average particle size is preferably from 1 to 30 μm, more preferably from 5 to 20 μm, still more preferably from 6 to 15 μm. From the viewpoint of inhibiting the aggregation of the detergent granules, the smaller the average particle size of the tripolyphosphate, the smaller the average particle size of the detergent granules. From the viewpoint of the productivity for preparing the detergent granules with small particle sizes on an industrial scale, the average particle size of the tripolyphosphate is preferably 1 μm or more, and from the viewpoint of inhibiting the aggregation of the detergent granules, the average particle size is preferably 30 μm or less. Here, the average particle size of the tripolyphosphate as referred to in the present specification is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.).

The optional ingredients which are added in step (A) or step (a) are preferably those in a granular or powdery state, and those prepared by pulverizing a lumpy mass, or those which are separately granulated may be used. The average particle size of the optional ingredients is preferably 200 μm or less. Incidentally, the optional ingredients may be added as an aqueous solution, paste or slurry. However, in order to prevent excessive aggregation, when water is

contained, its amount is preferably adjusted so as not to exceed the water content described below.

When the above optional ingredients are added, it is preferable that the optional ingredients are previously blended with the water-soluble, alkali inorganic substance before neutralizing in step (A) or step (a). The extent of mixing is preferably such that each of the ingredients is uniformly mixed. For instance, when an agitation granulator is used, it is preferable that the operation conditions for the agitation granulator are, for instance, a mixing time period of within 5 minutes.

In step (A) or step (a), water may be added for the purpose of accelerating the neutralization reaction. The amount of water added is preferably from 0.2 to 3 parts by weight, more preferably from 0.5 to 1.5 parts by weight, based on 100 parts by weight of the water-soluble, alkali inorganic substance (and in a case where optional ingredients are added, their weights on dry basis are added) in step (A) or step (a). The amount of water is preferably 0.2 parts by weight or more, from the viewpoint of initiating the neutralization reaction, and the amount is preferably 3 parts by weight or less, from the viewpoint of suppressing the aggregation of the detergent granules. Incidentally, in a case where water is contained in the components such as the liquid acid precursor of an anionic surfactant, or other water-soluble raw materials are used, or powder raw materials containing water are used, the amount of water to be added may be determined in consideration of these water contents.

In addition, as a more preferable embodiment for accelerating the neutralization reaction, an aqueous alkali solution or an alkali slurry solution (hereinafter simply referred to as “alkali solution”) can be preferably used in

place of water mentioned above. By using the alkali solution, not only the neutralization reaction can be more accelerated as compared to the case of using water, but also the particle size of the resulting detergent granules can be made small, whereby the bulk density can be markedly increased.

The alkali solution is added in an amount of preferably from 0.05 to 0.5 times the equivalent amount required for neutralization of the liquid acid precursor of an anionic surfactant, more preferably from 0.10 to 0.45 times the equivalent amount required for neutralization, especially preferably from 0.10 to 0.40 times the equivalent amount required for neutralization. From the viewpoint of initiating the neutralization reaction to obtain desired effects, the amount is preferably 0.05 times or more the equivalent amount required for neutralization, and from the viewpoint of suppressing the aggregation of the detergent granules, the amount is preferably 0.5 times or less the equivalent amount required for neutralization. Incidentally, in a case where the alkali solution has a low concentration, an excess amount of water is supplied to the mixture along with the addition of a given amount of the alkali solution, so that the aggregation of the detergent granules is likely to take place. Therefore, the concentration of the alkali solution is preferably from 20 to 50% by weight, more preferably from 30 to 50% by weight, especially preferably from 40 to 50% by weight.

In addition, the kinds of the alkalizing agent used in the alkali solution include strongly alkali aqueous solutions, such as aqueous sodium hydroxide and aqueous potassium hydroxide, which can readily cause the neutralization reaction with the liquid acid precursor of an anionic surfactant. Among them, the aqueous sodium hydroxide is favorably used from the viewpoint of costs.

The alkali aqueous solution more preferably has a pH of 12 or more, and it is preferable that the alkali solution is added by spraying or dropping to an extent that the alkali solution uniformly disperses when added. It is preferable that the alkali solution is added to a mixture of a water-soluble, alkali inorganic substance and other optional ingredients before blending with the liquid acid precursor of an anionic surfactant.

When the neutralization reaction is carried out in step (A) or step (a), it is preferable to previously add an inorganic acid, for example, sulfuric acid, and the like, to the liquid acid precursor of an anionic surfactant. In the granules obtained by neutralization reaction of a powdery or granular, water-soluble, alkali inorganic substance by using the mixture prepared by previously mixing the inorganic acid with the liquid acid precursor of an anionic surfactant, since a neutralized salt derived from the inorganic acid is present more near the granular surface than in the inner portion of the granules, the resulting granules have low adhesiveness and small particle sizes, whereby the granules having a high surfactant content can be prepared without causing the aggregation of the granules. In addition, since the granules obtainable in the manner described above have a large number of micropores, the granules having a high content of liquid ingredients, such as a nonionic surfactant, can be prepared. The inorganic acid is added in an amount of preferably from 0.1 to 1.0 moles, more preferably from 0.1 to 0.8 moles, still more preferably from 0.15 to 0.75 moles, especially preferably from 0.2 to 0.7 moles, most preferably from 0.25 to 0.65 moles, per one mol of the liquid acid precursor of an anionic surfactant. It is preferable that the inorganic acid is added in an amount of 0.1 moles or more, per one mol of the liquid acid precursor, from the viewpoint of suppressing the formation of

coarse grains of the detergent granules, and that the inorganic acid is added in an amount of preferably 1.0 mole or less, per one mol of the liquid acid precursor, from the viewpoint of securing the degree of freedom in the formulation composition of the concentrated detergent.

In step (A) or step (a), the order of adding the liquid acid precursor of an anionic surfactant and the water-soluble, alkali inorganic substance is not particularly specified. It is preferable that the liquid acid precursor is added to the water-soluble, alkali inorganic substance.

The method of adding the liquid acid precursor of an anionic surfactant may be carried out continuously or in a plurality of batches, and the plural addition means may be provided.

It is preferable that the neutralization process in step (A) or step (a) is carried out by using an agitation granulator. It is preferred that the agitation granulators are equipped with agitation blades and a chopper for disintegration and dispersion (or those replaced with a functionally equivalent means).

Concrete examples of the agitation granulators usable in the present invention for a batch process include Vertical Granulator (commercially available from Powrex Corp.); High-Speed Mixer (commercially available from Fukae Powtec Kogyo Corp.); Lödige Mixer (commercially available from Matsuzaka Giken Co., Ltd.); and PLOUGH SHARE Mixer (commercially available from PACIFIC MACHINERY & ENGINEERING Co., LTD.); Gericke Mixer (commercially available from Meiji Machine Co., Ltd.), and the like, and the Lödige Mixer and the PLOUGH SHARE Mixer are especially preferable. Concrete examples of the agitation granulators usable for a continuous process include continuous Lödige Mixer (moderate speed mixer:

those having relatively long residence time); high-speed mixer (those having relatively short residence time) such as CB recycler (commercially available from Lödige); Turbilizer (commercially available from Hosokawa Micron Corporation); Shugi Mixer (commercially available from Powrex Corp.); Flow Jet Mixer (commercially available from Funken Powtechs, Inc.), and the like. Incidentally, in the present invention, the above mixers may be appropriately used in combination. For instance, the neutralization reaction by the blending of the water-soluble, alkali inorganic substance and other optional ingredients and the neutralization reaction by the addition of the liquid acid precursor of an anionic surfactant may be treated in different agitation granulators.

It is more preferred that the agitation granulator used in the present invention is equipped with a jacket for adjusting the internal temperature of the granulator or is equipped with a nozzle for blowing a gas into the agitation granulator. Concrete examples of the more preferable agitation granulators include those mixers disclosed in Japanese Patent Laid-Open Nos. Hei 10-296064 and Hei 10-296065.

In addition, in step (A) or step (a), it is preferred that the neutralization is carried out while blowing a gas into an agitation granulator. By blowing a gas into the agitation granulator, the excess water produced in the neutralization reaction can be evaporated and the resulting granular product can be cooled with the gas, to thereby inhibit the granular product from forming into a doughy mass. The gases which may be usable include an N_2 gas, air, and the like. The amount of gas blown (amount of gas flow) is not particularly limited. The gas is blown at a rate of preferably equal to or greater than 0.002 parts by weight per minute, more preferably equal to or greater than 0.02 parts by weight per minute, based

on 100 parts by weight of the granular product.

The mixture comprising the neutralization substance of the acid precursor of an anionic surfactant obtainable in step (A) or step (a) as described above (in step (A), however, a non-neutralized acid precursor of an anionic surfactant can be also included), and the remaining water-soluble, alkali inorganic substance and other optional ingredients (hereinafter referred to as "neutralization mixture") is in a powdery or lumpy state. Especially when a detergent containing a surfactant in a ratio exceeding 20% by weight to the final detergent composition is prepared, the detergent granules are likely to form coarse grains or become lumpy, so that it is preferable to provide a disintegration process for the purpose of obtaining a detergent composition having a small particle size. Concretely, when the content of the anionic surfactant is 30% by weight or more, of the neutralization mixture, it is preferable to provide the disintegration process.

The method for disintegration may be carried out subsequently to step (A) or step (a) in the agitation granulator equipped with agitation blades and a chopper for disintegration and dispersion, or the method may be carried out by a separate disintegrator. Concrete examples of the disintegrator include Fitz Mill (commercially available from Hosokawa Micron Corporation), Speed Mill (commercially available from Okada Seiko K.K.), and the like.

2. Step (B) or step (b)

2-1. Step (B)

Step (B) comprises adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of a neutralization mixture obtained during a course of a neutralization process in

step (A) and mixing a resulting mixture. By initiating the addition of the inorganic powder at this point, there can be exhibited an effect of accelerating the disintegration effect of the neutralization mixture.

It is desired that the addition of the inorganic powder is initiated at any time after a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25, preferably an amount exceeding a weight ratio of 0.3, to the water-soluble, alkali inorganic substance. This is because the formation of coarse grains of the neutralization mixture is initiated at this point. Further, from the viewpoint of suppressing the compactification and the formation of coarse grains of the neutralization mixture by the progress of the granulation after the termination of the neutralization, it is desired that the inorganic powder is added within a short time period from the termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant, for instance, within 5 minutes. Within the above range, the disintegration of the neutralization mixture can be facilitated by initiating the addition of the inorganic powder within this range.

It is desired that the inorganic powder usable in step (B) has an average particle size of 30 μm or less, preferably 20 μm or less, from the viewpoint of suppressing the aggregation of the detergent granules. Here, the average particle size of the inorganic powder is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.). Examples of the inorganic powder include inorganic powdery builders and fine granular components generally usable in detergent compositions. Concrete examples thereof include alkali metal aluminosilicates, tripolyphosphates, crystalline

silicates, sodium sulfate, calcite, diatomaceous earth, silica, and the like. The inorganic powders may be used in combination of two or more kinds. Among these inorganic powders, from the viewpoint of the disintegration efficiency, the alkali metal aluminosilicate is especially preferable.

The alkali metal aluminosilicate may be either amorphous or crystalline, and those having a metal ion capturing ability as a detergent aid are preferable, and especially those generally so-called "synthetic zeolite" in the field of detergent are preferable. The alkali metal aluminosilicate has an average particle size of preferably from 1 to 30 μm, more preferably from 10 μm or less.

Especially in step (B), in a case where the alkali metal aluminosilicate is added, it is preferable that the alkali metal aluminosilicate is added at any point after the termination of the addition of an entire amount of the liquid acid precursor of an anionic surfactant, preferably after any point between a point where the agitation granulator is operated for additional 30 seconds or more, more preferably 1 minute or more, and a point up to 5 minutes from the termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant. By operating the agitation granulator after the termination of the addition of the liquid acid precursor, the neutralization reaction can be favorably completed. According to the above process, since the liquid acid precursor of an anionic surfactant is already neutralized, its deterioration and aggregation would not take place even if the alkali metal aluminosilicate were added. Therefore, the lowering of the detergency performance of the resulting detergent composition can be suppressed, so that there can be sufficiently exhibited an effect by the addition of the alkali metal aluminosilicate, namely the effect of improving the metal ion capturing ability and the supporting ability of

the liquid ingredients.

2-2. Step (b)

Step (b) comprises adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

The neutralization mixture obtained in step (a) referred to herein is a mixture in which an entire amount of the liquid acid precursor of an anionic surfactant is added, and it is preferable those in which the neutralization is terminated. In addition, the alkali metal aluminosilicate usable in step (b) may be the same ones as those of step (B).

In step (b), it is preferable that the addition of the alkali metal aluminosilicate is initiated in step (b) at any time within 5 minutes from the termination of the addition of an entire amount of the liquid acid precursor of an anionic surfactant, from the viewpoint of suppressing the compactification and the formation of coarse grains of the neutralization mixture by the progress of the granulation after the termination of the neutralization process. Especially, it is preferable that the alkali metal aluminosilicate is added at any point after the termination of the addition of an entire amount of the liquid acid precursor of an anionic surfactant, preferably after any point between a point where the agitation granulator is operated for additional 30 seconds or more, more preferably 1 minute or more, and a point up to 5 minutes from the termination of the addition of an entire amount of the liquid acid precursor of an anionic surfactant. By operating the agitation granulator after the termination of the addition of the liquid acid precursor, the neutralization reaction can be favorably completed. According to the above process, since the liquid acid precursor of an anionic

surfactant is already neutralized, its deterioration and aggregation would not take place even if the alkali metal aluminosilicate were added. Therefore, the lowering of the detergency performance of the resulting detergent composition can be suppressed, so that there can be sufficiently exhibited an effect by the addition of the alkali metal aluminosilicate, namely the effect of improving the metal ion capturing ability and the supporting ability of the liquid ingredients.

2-3. Others

The amount of the inorganic powder usable in step (B) or the alkali metal aluminosilicate usable in step (b) is preferably from 5 to 50% by weight, more preferably from 8 to 40% by weight, especially preferably from 10 to 36% by weight, of the high-bulk density detergent composition, which is the final product. From the viewpoint of suppressing the aggregation of the neutralization mixture, the amount is preferably 5% by weight or more, and from the viewpoint of securing the degree of compositional freedom of the resulting detergent composition, the amount is preferably 50% by weight or less.

In addition, a method of adding an inorganic powder or alkali metal aluminosilicate includes adding it at once or in a plurality of divided portions. Embodiments for adding in a plurality of divided portions include (i) an embodiment of adding an inorganic powder or alkali metal aluminosilicate for the purpose of facilitating disintegration when the neutralization mixture obtained in step (A) or step (a) is formed into coarse grains or lumpy masses (addition as a disintegration aid); (ii) an embodiment of adding an inorganic powder or alkali metal aluminosilicate for the purpose of adjusting the granulation property when adding the liquid binder described below (addition as

a granulation adjustment agent); and (iii) an embodiment of adding an inorganic powder or alkali metal aluminosilicate before the surface modification of the finally obtained detergent granules (addition as a surface modifier).

In step (B) or step (b), from the viewpoints of the reduction of fine powder and the improvements in the detergency and the metal ion capturing ability, it is desirable to formulate a liquid binder. According to the process of the present invention, the neutralization mixture can be made to have a small particle size, so that greater amounts of the liquid binder can be formulated.

The term "liquid binder" in the present invention refers to a substance imparting a property of increasing the bulk density of the detergent composition by collectively assembling the granules by the formulation of the liquid binder. The liquid binder includes, for instance, optional liquid ingredients in the detergent composition such as water, liquid nonionic surfactants, aqueous solutions of water-soluble polymers (polyethylene glycols, acrylic acid-maleic acid copolymers, and the like), and fatty acids. These liquid binders may be used in combination of two or more kinds, and embodiments of such addition methods include (1) adding after previously mixing two or more liquid binders; (2) simultaneously adding each of the liquid binders; and (3) alternately adding each of the liquid binders. In any of these methods, from the viewpoints of cost reduction, it is preferable to use water in combination. The amount of the liquid binder formulated is preferably 20 parts by weight or less, more preferably 15 parts by weight or less, based on 100 parts by weight of the neutralization mixture, from the viewpoint of suppressing the aggregation of the detergent composition.

The method of adding the liquid binder may be carried out continuously

or in a plurality of batches. It is preferable that the liquid binder is added to the neutralization mixture obtained in step (A) or step (a) before or after the addition of the inorganic powder. By the addition of the liquid binder at this stage, the adhesiveness of the granular surface by the liquid binder can be reduced, whereby the granulation can be suppressed. In the process of the present invention, besides adding a part of or all of optional ingredients in step (A) or step (a), the optional ingredients can also be formulated in step (B) or step (b). Especially when the above aqueous solution of the water-soluble polymer is used, it is preferable to add the aqueous solution in step (B) or step (b) rather than in step (A) or step (a), from the viewpoint of granulation property. In this case, the inorganic powder can be added in plural batches as shown in the above embodiments (i) to (iii), so that the granulation property is not greatly affected by the water content carried by the optional ingredients into the neutralization mixture.

In the process of the present invention, it is preferable to provide a surface-modifying step as shown in the above embodiment (iii). The surface modification step can be also carried out by using the inorganic powder such as an alkali metal aluminosilicate. By adding the inorganic powder to detergent granules in which the granulation is proceeded to a certain extent and surface-coating the detergent granules, the powder properties such as anti-caking property and flowability can be improved.

It is desired that the amount of the surface modifier is from 2 to 15% by weight, preferably from 4 to 12% by weight, of the detergent composition after the surface modification.

Incidentally, in the present invention, in a case where other volatile

compounds or thermally sensitive optional ingredients are added, such components may be added after at a point where at least the first batch of the inorganic powder or alkali metal aluminosilicate is added in step (B) or step (b) in the present invention, and the particle sizes are evenly sized, or these components may be after-blended by mixing the granules finally treated with a surface-coating agent by using a mixer such as a rotary mixer.

The high-bulk density detergent composition obtained by the process of the present invention may be used as ingredients for constituting other detergent compositions.

In addition, the process of the present invention can be carried out by a continuous process. In this case, step (A) or step (a) can be carried out using, for instance, a high-speed mixer such as CB recycler, and thereafter, step (B) or step (b) can be carried out using, for instance, a moderate-speed mixer such as continuous Lödige Mixer.

According to the process described above, a high-bulk density detergent composition comprising a granular mixture having a bulk density of 650 g/L or more, the detergent composition having excellent detergency and a small average particle size, can be obtained.

It is more preferable that the high-bulk density detergent composition obtained by the process of the present invention has the following properties.

Average particle size: Measured by vibrating a sample with each of standard sieves according to JIS Z 8801 for 5 minutes, and thereafter determining from a weight percentage depending upon the size openings of the sieves. The average particle size is preferably 700 μm or less, more preferably 650 μm or less.

Bulk density: Preferably from 650 to 950 g/L, more preferably from 700 to 900 g/L. Here, in the present specification, the bulk density is measured by a method according to JIS K 3362.

Flowability: The flowability of the detergent composition in the present specification is expressed as flow time which is defined as a time period required for dropping 100 mL of a powdery detergent composition from a hopper used in the determination of the bulk density according to JIS K 3362. The flow time is preferably 8 seconds or shorter, more preferably 7 seconds or shorter.

Detergency: The detergency is expressed a relative detergency ratio. The relative detergency ratio is preferably 0.95 or more, more preferably 0.98 or more. The more the relative detergency ratio approximates 1, the less the affect of the process to individual ingredients. Incidentally, in the present invention, the relative detergency ratio is obtained as follows.

First, a detergent composition to be tested is dissolved in water, to give an aqueous solution of the detergent composition. This solution is referred to as "test detergent aqueous solution." Next, an aqueous solution having the same composition as the test detergent aqueous solution is obtained by adding and mixing the individual ingredients constituting the detergent composition with water. This aqueous solution is referred to as "control detergent aqueous solution." The detergency of the test detergent aqueous solution and the detergency of the control detergent aqueous solution are obtained by the following detergency test. Thereafter, the relative detergency ratio is obtained by:

$$\text{Relative Detergency Ratio} = \frac{\text{Detergency of Test Detergent Aqueous Solution}}{\text{Detergency of Control Detergent Aqueous Solution}}$$

<Detergency of Detergent>

(Preparation of Artificial Stained Cloth)

An artificially stained cloth is prepared by smearing an artificial soil solution having the composition shown in Table 1 to a cloth. The smearing of the artificial soil solution to a cloth is carried out in accordance with Japanese Patent Laid-Open No. 7-270395 wherein the artificial soil solution was printed on a cloth by a gravure staining machine equipped with a gravure roll coater. The conditions for smearing the artificial soil solution to a cloth to prepare an artificially stained cloth are a cell capacity of a gravure roll of 58 cm^3/cm^2, a coating speed of 1.0 m/min, a drying temperature of 100°C, and a drying time of one minute. As to the cloths, #2003 calico (manufactured by Tanigashira Shoten) is used.

Table 1

Lauric Acid	0.44% by weight
Myristic Acid	3.09% by weight
Pentadecanoic Acid	2.31% by weight
Palmitic Acid	6.18% by weight
Heptadecanoic Acid	0.44% by weight
Stearic Acid	1.57% by weight
Oleic Acid	7.75% by weight
Triolein	13.06% by weight
n-Hexadecyl Palmitate	2.18% by weight
Squalene	6.53% by weight
Lecithin, from Egg White	1.94% by weight
Kanuma Red Clay	8.11 by weight
Carbon Black	0.01 by weight
Tap Water	Balance

(Detergent Conditions and Evaluation Method)

Five pieces of the artificially stained cloths of 10 cm x 10 cm prepared above are placed in one liter of an aqueous solution for measurement detergent or that of control detergent and washed with turgotometer at 100 rotations/min. The washing conditions are concretely as follows: the washing time: 10 minutes, the detergent concentration: 0.083% by weight; water hardness: 5°DH; water temperature: 20°C; rinsing: with tap water for 5 minutes.

The detergency was evaluated by measuring the reflectance at 550 nm of the original cloth before staining and those of the stained cloth before and after washing by an automatic recording colorimeter (manufactured by SHIMADZU

CORPORATION), and the detergency (%) was calculated by the following equation. The average value determined of 5 pieces was expressed as the detergency (%).

$$\text{Detergency (\%)} = \frac{\text{Reflectance After Washing} - \text{Reflectance Before Washing}}{\text{Reflectance of Original Cloth} - \text{Reflectance Before Washing}} \times 100$$

In the subsequent Examples, as the zeolite, there was used Zeolite 4A (manufactured by Tosoh Corporation); as the nonionic surfactant, there was used a polyoxyethylene alkyl ether (prepared by adding ethylene oxide in an average of 8 moles to a primary alcohol of which alkyl moiety has 12 to 14 carbon atoms (average being 12.8)); as a fatty acid, there was used palmitic acid; and as the acrylic acid-maleic acid copolymer, there was used one having a weight-average molecular weight of about 70000 as determined by gel permeation method using a polyethylene glycol as a standard.

Example 1

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer was equipped with agitator blades; a shearing device corresponding to a chopper for disintegration and dispersion; and a jacket for adjusting the temperature within the mixer.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 13.19 parts by weight of sodium carbonate ("LIGHT ASH," manufactured by Central Glass Co., Ltd.; average particle size: 56.1 μm), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the conditions of a rotational speed of agitator blades of 130 rotations/min (peripheral speed: 3.4 m/s) and a rotational speed of a shearing device of 2850 rotations/min (peripheral speed: 27 m/s).

<Neutralization>

While the mixer was operated under the same conditions as above, 9.40 parts of by weight of a linear alkylbenzenesulfonic acid (LAS; molecular weight: 322) was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the LAS, the temperature inside the mixer rose to 75°C in the highest. After the addition of the LAS, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the LAS, the aeration within the mixer (300 L/min) was carried out.

<Addition of Alkali Metal Aluminosilicate>

At a point where the neutralization reaction and granulation process were completed, a zeolite (5.00 parts by weight) having an average particle size of

4 μm was added, while the mixer was operated under the same conditions as above, and mixing was carried out for 5 minutes.

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4 μm was added thereto, and blended for additional 5 minutes. Thereafter, a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to a surface modification treatment by adding the zeolite (3.50 parts by weight) having an average particle size of 4 μm to the mixer as a surface modifier, and operating the mixer for additional one minute.

The granules of the resulting detergent composition had an average particle size of 640 μm, a bulk density of 795 g/L, and a flowability of 7.1 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.998, whereby showing excellent detergency.

<After-Blending>

Using a rotary mixer, an enzyme (0.18 parts by weight) and the detergent composition obtained above were mixed, and a perfume (0.07 parts by weight) was further sprayed thereto, to give a final powder of the high-bulk density detergent composition.

Example 2

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 12.88 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 9.40 parts of by weight of the LAS and 0.84 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 80°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

<Addition of Alkali Metal Aluminosilicate>

In the same manner as in Example 1, a zeolite (5.00 parts by weight) having an average particle size of 4 µm was added, and mixing was carried out for 5 minutes.

<Addition of Liquid Ingredients and Surface Modification>

In the same manner as in Example 1, the nonionic surfactant (0.98 parts by weight), the zeolite (2.00 parts by weight) having an average particle size of 4 µm, and the 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) were added to the mixer, and the ingredients were blended. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 565 µm, a bulk density of 776 g/L, and a flowability of 7.3 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.988, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

Example 3

A detergent composition was obtained by using the same composition and the operations as employed in Example 2, except for changing the amount of LIGHT ASH used to 12.73 parts by weight, adding 0.23 parts by weight of a 48% by weight aqueous NaOH solution as a reaction initiating agent before neutralization to the mixture of LIGHT ASH and a fluorescer, and thereafter adding a process for blending for 1 minute and 30 seconds under the same conditions as those for the process of powder blending.

The granules of the resulting detergent composition had an average particle size of 550 μm, a bulk density of 780 g/L, and a flowability of 7.3 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.990, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

<u>Example 4</u>

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer “FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 12.22 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 7.39 parts of by weight of the LAS and 0.87 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 75°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out. Subsequently, 0.97 parts by weight of a fatty acid was added in 30 seconds, and thereafter, the ingredients were mixed for one minute.

<Addition of Alkali Metal Aluminosilicate>

In the same manner as in Example 1, a zeolite (6.05 parts by weight) having an average particle size of 4 μm was added, and mixing was carried out for 5 minutes.

<Addition of Liquid Ingredients and Surface Modification>

In the same manner as in Example 1, the nonionic surfactant (1.51 parts by weight), the zeolite (2.00 parts by weight) having an average particle size of 4 μm, and the 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) were added to the mixer, and the ingredients were blended. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 510 μm, a bulk density of 778 g/L, and a flowability of 6.5 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.988, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

Example 5

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 11.00 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 11.76 parts of by weight of the LAS and 1.05 parts by weight of 98% sulfuric acid was added to the mixer in 5 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 85°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 4 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

<Addition and Disintegration of Alkali Metal Aluminosilicate>

While the mixer was operated under the same conditions as above, a zeolite (5.00 parts by weight) having an average particle size of 4 μm was added as a disintegration aid, and mixing was carried out for 5 minutes. Thereafter, the mixture was disintegrated using a Fitz Mill (manufactured by Hosokawa Micron Corporation).

<Addition of Liquid Ingredients and Surface Modification>

While the disintegrated mixture was stirred in the above Lödige Mixer under the same conditions as above, the nonionic surfactant (0.70 parts by weight) was added to the mixer and blended for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4 μm was added thereto, and blended for additional 5 minutes. Thereafter, a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 560 μm, a bulk density of 780 g/L, and a flowability of 7.4 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.994, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

<u>Comparative Example 1</u>

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had

the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 13.19 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), 7.00 parts by weight of a zeolite having an average particle size of 4 μm, and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

While the mixer was operated under the same conditions as above, 9.40 parts of by weight of the LAS was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the LAS, the temperature inside the mixer rose to 75°C in the highest. After the addition of the LAS, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the LAS, the aeration within the mixer (300 L/min) was carried out.

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended for one minute, and thereafter a 40% by weight aqueous solution of acrylic acid-

maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 650 μm, a bulk density of 770 g/L, and a flowability of 6.9 seconds, whereby showing excellent powder properties. However, the granules had a relative ratio for the detergency rate of 0.902, whereby showing notably poorer detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the detergent composition.

Table 2

	Example No.					Comp. Ex. No.
	1	2	3	4	5	1
Composition (% by weight)						
LAS-Na	28.00	28.00	28.00	22.00	35.00	28.00
Soap	0.00	0.00	0.00	3.00	0.00	0.00
Zeolite	30.00	30.00	30.00	33.00	30.00	30.00
Sodium Carbonate	33.00	29.50	29.50	28.00	22.30	33.00
Sodium Sulfate	0.50	4.00	4.00	4.00	5.00	0.50
Copolymer*	1.70	1.70	1.70	1.70	1.70	1.70
Nonionic**	2.80	2.80	2.80	4.30	2.00	2.80
Fluorescer	0.30	0.30	0.30	0.30	0.30	0.30
Enzyme	0.50	0.50	0.50	0.50	0.50	0.50
Perfume	0.20	0.20	0.20	0.20	0.20	0.20
Water	3.00	3.00	3.00	3.00	3.00	3.00
Total	100.00	100.00	100.00	100.00	100.00	100.00

*: Acrylic acid-maleic acid copolymer.
**: Nonionic surfactant.

Examples 6 to 8 and Comparative Example 2

A detergent composition having a composition shown in Table 3 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows (the amount of each raw material formulated in each step is shown in Table 4).

<Powder Blending>

Solid ingredients, comprising sodium carbonate ("LIGHT ASH," manufactured by Central Glass Co., Ltd.; average particle size: 56.1 μm), sodium tripolyphosphate (STPP; average particle size: 11.2 μm), and a fluorescer, were blended for one minute with the above Lödige Mixer under the conditions of a rotational speed of agitator blades of 130 rotations/min (peripheral speed: 3.4 m/s) and a rotational speed of a shearing device of 2850 rotations/min (peripheral speed: 27 m/s).

<Addition of Reaction Initiating Agent>

A 48% by weight of NaOH aqueous solution was added to the contents in the mixer as a reaction initiating agent, and the blending was carried out for 1 minute and 30 seconds under the same conditions as above.

<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 9.40 parts of by weight of the LAS and 0.84 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 75°C in the highest. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

<Blending of Inorganic Powder >

An inorganic powder (1.75 parts by weight) was added to the resulting neutralized mixture, and the mixer was continuously operated under the same conditions as above for 4 minutes and 30 seconds.

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4 μm was added thereto, and blended for additional 5 minutes. Thereafter, a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to a surface modification treatment by adding the zeolite (2.20 parts by weight) having an average particle size of 4 μm to the mixer as a surface modifier, and operating the mixer for additional one minute.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density granular detergent composition.

Here, in Example 6 or 7, after 30 seconds from the termination of addition of the LAS, STPP or zeolite (1.75 parts by weight) was added as an inorganic

powder. In addition, in Example 8, the addition of STPP, an inorganic powder was carried out during the course of the neutralization process, and the mixture was continued to be blended for 5 minutes after termination of the addition of the LAS. Incidentally, the addition of STPP was carried out at a point where a weight ratio of the LAS added to sodium carbonate reached 0.6. In Comparative Example 2, the mixture was blended for 5 minutes after the termination of the addition of LAS, without adding an inorganic powder during the course of the neutralization process or immediately after the neutralization process.

The properties of each of the resulting high-density detergent composition are shown in Table 5.

Table 3

	Example No.				Comp. Ex. No.
	6	7	8	9	2
Composition (% by weight)					
LAS-Na	28.00	28.00	28.00	28.00	28.00
Zeolite	12.00	17.00	12.00	12.00	12.00
STPP	20.00	15.00	20.00	20.00	20.00
Sodium Carbonate	27.50	27.50	27.50	28.80	27.50
Sodium Sulfate	4.00	4.00	4.00	4.00	4.00
Copolymer*	1.70	1.70	1.70	1.70	1.70
Nonionic**	2.80	2.80	2.80	–	2.80
Fluorescer	0.30	0.30	0.30	0.30	0.30
Enzyme	0.50	0.50	0.50	0.50	0.50
Perfume	0.20	0.20	0.20	0.20	0.20
Water	3.00	3.00	3.00	4.50	3.00
Total	100.00	100.00	100.00	100.00	100.00

*: Acrylic acid-maleic acid copolymer.
**: Nonionic surfactant.

Table 4

Composition (parts by weight)	Example No.				Comp. Ex. No.
	6	7	8	9	2
<Powder Blending>					
Sodium Carbonate	12.03	12.03	12.03	12.48	12.03
Sodium Tripolyphosphate	5.25	5.25	5.25	5.25	7.00
Fluorescer	0.11	0.11	0.11	0.11	0.11
<Addition of Reaction Initiating Agent>					
48% by weight NaOH	0.23	0.23	0.23	0.23	0.23
<Neutralization>					
Linear Alkylbenzene-sulfonic Acid (LAS)	9.40	9.40	9.40	9.40	9.40
98% Sulfuric Acid (Amount of Air Flow [L/min])	0.84 300	0.84 300	0.84 300	0.84 300	0.84 300
<Blending of Inorganic Powder>					
Sodium Tripolyphosphate	1.75	–	1.75	–	–
Zeolite	–	1.75	–	3.75	–
<Addition of Liquid Ingredients and Surface Modification>					
Nonionic Surfactant	0.98	0.98	0.98	–	0.98
Zeolite	2.00	2.00	2.00	–	2.00
Water	–	–	–	0.53	–
Acrylic Acid-Maleic Acid Copolymer (Effective Ingredient)	1.49	1.49	1.49	1.49	1.49
Zeolite for Surface Modification	2.20	2.20	2.20	2.20	2.20
<After-Blending>					
Enzyme	0.18	0.18	0.18	0.18	0.18
Perfume	0.07	0.07	0.07	0.07	0.07

Table 5

	Example No.				Comp. Ex. No.
	6	7	8	9	2
Final Average Particle Size (µm)	460	457	474	450	547
Average Particle Size (µm) Immediately After Acid Addition	465	458	460	453	440
Bulk Density (g/L)	753	756	764	755	783
Flowability (sec)	6.5	6.5	6.5	6.4	6.7
Ratio of Relative Detergency	0.997	0.988	0.996	0.996	0.997

It is clear from the above results of Table 5 that by adding an inorganic powder during the course or immediately after the neutralization process, the granular growth from the termination of the neutralization process can be suppressed, and consequently, there can be obtained a high-bulk density detergent composition not only having excellent detergency but also comprising granules having a small average particle size.

Example 9

A detergent composition having a composition shown in Table 3 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer “FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows (the amount of each raw material formulated in each step is shown in Table 4).

<Powder Blending>

Solid ingredients, comprising sodium carbonate (the same LIGHT ASH as in Example 1), sodium tripolyphosphate (the same STPP as in Example 6), and a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

While the mixer was operated under the same conditions as in Example 1, a mixture comprising 9.40 parts of by weight of the LAS and 0.84 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 80°C in the highest. After the completion of the addition of the mixture, the mixer was continuously operated under the same conditions for 30 seconds to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

<Addition of Alkali Metal Aluminosilicate>

Zeolite (3.75 parts by weight) was added to the resulting neutralized mixture, and the mixer was continuously operated under the same conditions as above for 4 minutes and 30 seconds.

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as in Example 1, a mixture comprising a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer and water was added to the mixer and blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to a surface modification treatment in the same manner as in Example 1.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density granular detergent composition.

The properties of the resulting high-bulk density detergent composition are shown in Table 5. It is clear from Table 5 that a high-bulk density detergent composition having excellent detergency and a small average particle size can be obtained.

INDUSTRIAL APPLICABILITY

According to the process of the present invention, a high-bulk density detergent composition having excellent detergency and a small average particle size can be obtained.

JC13 Rec'd PCT/PTO 20 FEB 2002

CLAIMS

1. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture.

2. The process according to claim 1, wherein the addition of the inorganic powder is initiated in step (B) at any time between a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25 to the water-soluble, alkali inorganic substance and a point up to 5 minutes from termination of addition of an entire amount of the liquid acid precursor.

3. The process according to claim 1 or 2, wherein the average particle size of the inorganic powder is 30 μm or less.

4. The process according to any one of claims 1 to 3, wherein the inorganic

powder is an alkali metal aluminosilicate.

5. The process according to claim 4, wherein the addition of the alkali metal aluminosilicate is initiated in step (B) at any time within 5 minutes from termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

6. The process according to any one of claims 1 to 5, wherein the alkali metal aluminosilicate is contained in step (A) in an amount of 5% by weight or less.

7. The process according to any one of claims 1 to 6, wherein the neutralization step is carried out in step (A) while blowing a gas.

8. The process according to any one of claims 1 to 7, wherein in step (B), a liquid binder is further added to the neutralization mixture obtained in step (A).

9. The process according to any one of claims 1 to 8, further comprising a surface-modifying step.

10. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a

substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

11. The process according to claim 10, wherein the addition of the alkali metal aluminosilicate is initiated in step (b) at any time within 5 minutes from termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

12. The process according to claim 10 or 11, wherein the alkali metal aluminosilicate is contained in step (a) in an amount of 5% by weight or less.

13. The process according to any one of claims 10 to 12, wherein the neutralization step is carried out in step (a) while blowing a gas.

14. The process according to any one of claims 10 to 13, wherein in step (b), a liquid binder is further added to the neutralization mixture obtained in step (a).

15. The process according to any one of claims 10 to 14, further comprising a surface-modifying step.

1422-0419P

Attorney Docket No.

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PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title: PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS

Fill in Appropriate Information - For Use Without Specification Attached:

the specification of which is attached hereto. If not attached hereto,
the specification was filed on ______ as
United States Application Number ______;
and amended on ______ (if applicable) and/or
the specification was filed on August 17, 2000 as PCT
International Application Number PCT/JP00/05487; and was
amended under PCT Article 19 on ______ (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representative or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

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Insert Priority Information: (if appropriate)

Prior Foreign Application(s) — **Priority Claimed**

(Number)	(Country)	(Month/Day/Year Filed)	Yes	No
11-234155	Japan	August 20, 1999	☒	☐
			☐	☐
			☐	☐
			☐	☐

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(Application Number)	(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More than 12 Months (6 Months for Designs) Prior to the Filing Date of This Application:

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Country	Application Number	Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States and/or PCT application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States and/or PCT application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to the patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Insert Prior U.S. Application(s): (if any)

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

1422-0519P
Attorney Docket No.

I hereby appoint the practitioners at **CUSTOMER NO. 2292** as my attorneys or agents to prosecute this application and/or an international application based on this application and to transact all business in the United States Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the practitioners, unless the inventor(s) or assignee provides said practitioners with a written notice to the contrary:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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